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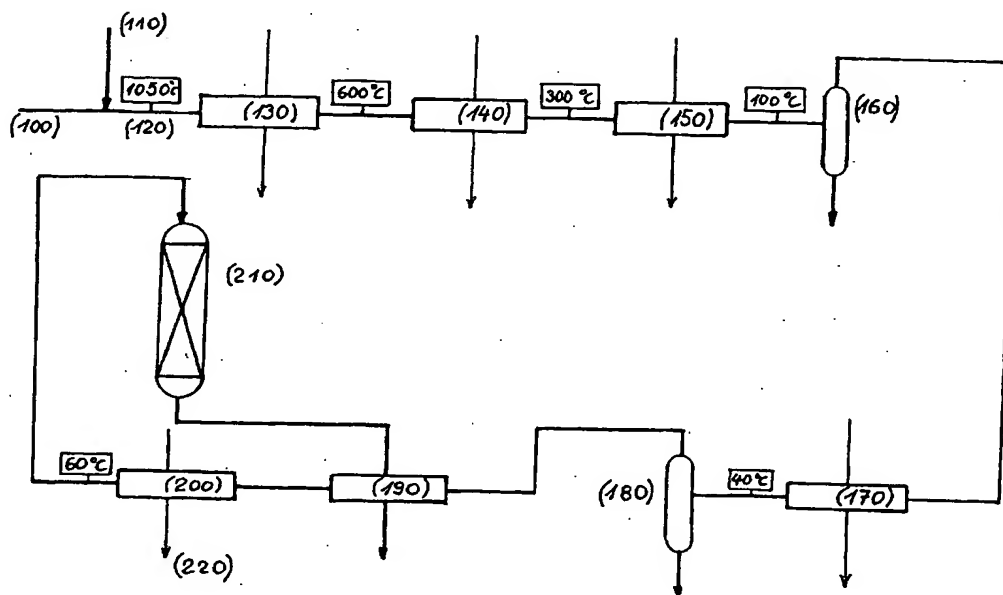
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(54) Title: PROCESS FOR THE SELECTIVE REMOVAL OF SULPHUR COMPOUNDS FROM SYNTHESIS GAS



(57) Abstract: A process for the selective removal of sulphur compounds from synthesis gas being rich in carbon monoxide and containing hydrogen, carbon monoxide and containing hydrogen, carbon dioxide and steam comprising contacting the synthesis gas at a maximum contact temperature of 100° C with an absorbent comprising Cu/ZnO compounds, and being prepared by thermal decomposition of a corresponding carbonate and activation of the thermal decomposed carbonate with a reducing gas.

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Process for the selective removal of sulphur compounds
from synthesis gas

This invention relates to a process for the selective removal of H_2S from synthesis gas being rich in carbon monoxide and further containing hydrogen, carbon dioxide and steam.

5

Selective removal is defined as a removal process being basically neutral with respect to the reactants contained in the synthesis gas, i.e. contents of other than impurities, steam and inert gas is not changed to any substantial degree. In addition, formation of components not already contained in the synthesis gas must be avoided. In praxis side-reactions must be suppressed to a level lower than 1000 vol ppm levels.

10

All concentrations given in present description are by volume.

15

H_2S and other sulphur compounds are poisonous to a wide range of catalysts e.g. nickel, iron and copper based catalysts fed with synthesis gas and used for synthesis in the industry. The catalysts are deactivated in contact with catalyst poisons contained in the gas. Sulphur compounds form stable compounds on the catalytic surface and block its active sites.

20

25

Therefore, selective removal of sulphur as defined above is industrially useful for removal of sulphur compounds downstream to reformers producing synthesis gas from hydrocarbons in chemical plants.

30

Examples, where downstream selective removal of sulphur compounds from synthesis gas is useful, include removal of

H₂S and COS from synthesis gas generated in high temperature autothermal reformers. In an autothermal reformer sulphur may be acceptable in the hydrocarbon feed and all sulphur in the feed will be converted to H₂S and minor amounts of COS.

As the catalysts in the downstream synthesis section are susceptible to sulphur poisoning, sulphur must be removed to the low ppb level (<5 ppb). The sulphur removal is to be obtained either at inlet to the synthesis gas preparation section upstream to the reformer, or alternatively downstream to the reformer, in case the synthesis gas preparation section is tolerant to sulphur.

When downstream removal of sulphur compounds is applied, the removal process must fulfil certain requirements in terms of selectivity. In general, it is not desired to change the composition of the synthesis gas generated.

Especially, components not already contained in the synthesis gas must not be formed, as these interfere in the synthesis section and in the purification of the final product.

Further, in general a loss of the content of carbon monoxide in the synthesis gas of more than 0.5% relative would in most cases be unacceptable due to process economics.

Furthermost, for some syntheses, for example in Fischer-Tropsch and oxo-alcohol synthesis, the ratio of the components H₂/CO in the synthesis gas is very critical, thus a

change in composition due to sulphur removal is unacceptable.

5 When operating the removal process in praxis, selective removal of sulphur requires reduction of sulphur concentration to below 5 ppb in the treated synthesis gas. The removal process shall affect only impurities, steam and inerts, and no more than about 1000 ppm of components already contained in the gas must be formed by the process.

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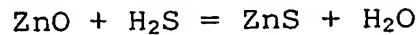
Synthesis gas generated in reformers comprises conventionally both substantial amounts of carbon monoxide, hydrogen, carbon dioxide, steam, various inert compounds and impurities. In other applications synthesis gas is generated with very low levels of carbon dioxide, such as coal gasifiers. By all means synthesis gas generated in either reformers or gasifiers is rich in carbon monoxide and further contains hydrogen, steam and more or less carbon dioxide.

20 Thus, the synthesis gas to be treated by selective removal of sulphur is rich in carbon monoxide and further contains hydrogen, carbon dioxide and steam.

25 The typical pressure of a synthesis gas exit the reformer, and accordingly the pressure level of interest of selective sulphur removal, is in the range 15-80 bar.

30 The most conventionally used means of H_2S removal from a gas stream is passing the gas through a bed of zinc oxide at elevated temperatures, typically from 300-450°C. Use of conventional zinc oxide absorbents is inappropriate in H_2S removal from wet synthesis gases being rich in carbon mon-

oxide. Steam decreases the efficiency of H₂S removal through the absorption reaction:



5

In wet synthesis gas sulphur content exceeds thus the sulphur tolerance limit of down stream catalysts. Further, ZnO absorbents are active catalysts in the water gas shift reaction at usual operating conditions.

10

Further common H₂S absorbents being based on nickel or copper, capable of reducing H₂S concentration to much lower levels cause unwanted side reactions like hydrocarbon formation, water gas shift and methanol synthesis.

15

EP 243,052 discloses agglomerates of copper and zinc and/or metals of Groups IIIA, IVA, VA, VIA and VIIA in form of oxides, hydroxides, carbonates and/or basic carbonates as useful sulphur absorbents in natural gas, NGL or liquid refinery products. The fluids to be treated are preferably free of reducing gases.

20

We have found that unreduced basic carbonates are not useful in sulphur removal from synthesis gas, because basic carbonates are reduced by the reducing synthesis gas at temperatures as low as 55°C. At 40°C the reduction of the absorbent is absent or progresses very slowly, however, minor operational upsets will lead to temperature increments initiating the reduction process resulting in detrimental temperatures run-away.

30

US Patent No. 4,521,387 relates to sulphur absorbents in form of a Cu/ZnO catalyst, which is prepared by thermal decomposition of $\text{Cu}_x\text{Zn}_y(\text{OH})_6(\text{CO}_3)_2$. The absorbent is employed in deep purification of synthesis gas for the removal of e.g. H_2S and other impurities at a temperature of 100°C .

Undesired side-reactions during removal of sulphur from synthesis gas by use of the above absorbents are not discussed in EP 243,052 and US Patent No. 4,521,387.

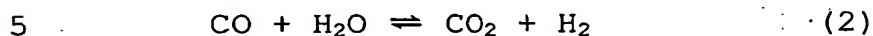
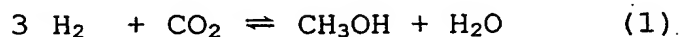
Furthermore, US Patent No. 4,521,387 does not describe examples of desulphurisation of synthesis gas containing CO, H_2 , steam and CO_2 . Example 3 of this reference discloses deep desulphurisation of a synthesis gas comprising CO and H_2 but no steam or CO_2 .

It is generally known that the absorbent applied in US Patent No. 4,521,387 catalyses the production of methanol predominantly through the activation of CO_2 .

Activation of CO_2 and CO for methanol synthesis are quite independent. It was first found by Rozovskii (Yu. B. Kagan et al, Dokl. Akad. Nauk SSR, 221, 1093, (1975)) by means of an isotope doping method that methanol is synthesised from CO_2 and not from CO over the Cu catalyst as present. The experiment was confirmed by Ken Waugh (G.C. Chinchin et al, appl. Catal., 36, 1-65, (1988)).

It is generally known that the absorbent applied in US Patent No. 4,521,387 also catalyses the water gas shift reaction.

Methanol synthesis and water gas shift reactions are catalysed according to the following reaction schemes:



It is known that a Cu/ZnO catalyst, if being active in reaction 1, is also active in reaction 2. Thus, any CO converted into methanol is converted through the shift reaction 2.

Due to the exothermic nature of the above reactions, the equilibrium conversion is decreasing with increasing temperature, thus the lower the equilibrium temperature the higher the equilibrium conversion.

Whether or not the catalysis through the above schemes takes place to any substantial degree (conversion corresponding to more than 1000 ppm methanol), depends apart from the catalytic activity also on the thermodynamic potential of the feed gas.

Below is given equilibrium concentrations of methanol and conversions of carbon monoxide according to reaction schemes 1 and 2 for a series of synthesis gas compositions.

Syngas composition A (Carbon dioxide composition from acid gas wash as per Example 2 of US Patent No. 4,521,387): 97.45% CO₂, 0.1% H₂ and 2.45% H₂O. Pressure=3 bar.

Syngas composition B (Synthesis gas composition from partial oxidation as per Example 3 of US Patent No. 4,521,387): 48.5% CO and 51.5% H₂. Pressure=21 bar.

5 Syngas composition C (Synthesis gas composition as per our Example 1): 49% H₂, 20% H₂O, 25% CO, 5% CO₂ and 1% CH₄. Pressure=31 bar. Cooled and separated at operating temperature of the sulphur removal unit.

10 Syngas composition D (Synthesis gas composition as per our Example 4): 70.48% H₂ (balance), 0.02% H₂O, 16.3% CO, 10.2% CO₂, 3.0% Ar. Pressure=21 bar.

15 Syngas composition E (Synthesis gas composition as per our Example 5, steam/dry gas ratio of 0.028): 70.53% H₂, 14.1% CO, 9.72% CO₂, 2.92% Ar, 2.72% H₂O. Pressure=21 bar.

Table 1

Potential for methanol and shift reactions.
Equilibrium concentrations and conversions.

20

Syngas Composition	Equilibrium Temperature [Deg. C]	Concentration of CH ₃ OH in effluent, [%]	Conversion of CO to CH ₃ OH, [%]	Conversion of CO by shift alone, [%]
A	100	<<0.1	÷, No CO in feed	÷ ^{**} , No CO in feed
B	100	0 [*] No CO ₂ or H ₂ O in feed	0 [*] No CO ₂ or H ₂ O in feed	0 No H ₂ O in feed
C	40/100	78/58	99.9/99.8 ^{***}	0.79/11
D	40/125	41/25	>99.9/>99.9 ^{***}	0.12/-0.05 low H ₂ O in feed
E	100	25	99.9 ^{***}	19

*) The equilibrium conversions to CH₃OH for Syngas B is calculated on the basis that the activation of CO does not take place on the catalyst: 2H₂ + CO ⇌ CH₃OH, as shown by Rozovskii.

25 **) Equilibrated gas contains 11 ppm of CO, build by reverse shift. The building of 11 ppm is far below the critical limit of the formation level of 1000 ppm of components not contained in the feed gas.

***) CO is converted into methanol via the water gas shift reaction as water is present in the feed.

Synthesis gas from downstream reformers typically contains more than 5% CO, at least 1% CO, and further contains H₂ and CO₂ (and the synthesis gas is typically saturated with steam at temperatures below 100°C).

5

In the pressure range 15-80 bar and at a temperature 15-100°C the thermodynamic potential for methanol synthesis of a gas containing at least 5% CO, at least 5% H₂, at least 0.5% CO₂ and optionally further containing water in a concentration up to saturation at a temperature of 100°C is more than 1000 ppm of methanol.

10

At higher pressure and/or lower temperature the potential for methanol synthesis in above composition increases.

15

Such synthesis gas has to be desulphurised over an absorbent not catalysing the methanol reaction at absorption conditions.

20

The general object of this invention is to provide an improved processes for selective removal of sulphur compounds from synthesis gas being rich in carbon monoxide and further containing both hydrogen, carbon dioxide and steam.

25

It has been found that an absorbent of reduced Cu/ZnO/Al₂O₃ removes H₂S and COS to below 5 ppb levels in such a synthesis gas with high sulphur capacity. It has also been observed that methanol synthesis does not occur at 40°C or at 125°C and that conversion of CO through the water gas shift

30

reaction is absent at 100°C or below.

Useful absorbents comprise Cu/ZnO compounds prepared by thermal decomposition of the respective carbonate and subsequent activation with reducing gas (e.g. H₂/N₂) and compositions of copper on ZnO carrier.

5

In accordance with the above object and observations, this invention is a process for the selective removal of sulphur compounds from synthesis gas containing at least 5% carbon monoxide, at least 5% hydrogen and at least 0.5% carbon di-
oxide and optionally further containing water in a concen-
tration up to saturation comprising contacting the synthe-
sis gas at a maximum contact temperature of 100°C with an
absorbent comprising Cu/ZnO compounds and being activated
with a reducing gas.

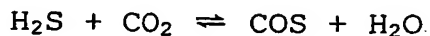
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An advantage of the reduced copper based absorbents, in which copper metal is active, is the ability to remain stable in synthesis gas rich in carbon monoxide even if exposed to higher temperatures.

20

In addition to absorption of H₂S reduced copper based absorbents are effective absorbents in removing COS being formed by side-reactions,

25



in the absorber or up-stream the absorber at certain process conditions.

30

In further an embodiment of the invention the absorbent is useful to remove sulphur being added to synthesis gas to

suppress metal dusting in chemical plants as described in more detail below.

5 Metal dusting corrosion is a well-known phenomenon in the chemical industry described in numerous publications. Metal dusting corrosion involves disintegration of metals and alloys into small particles of metal, metal carbides, metal oxides and carbon.

10 A key element of metal dusting is the transfer of carbon from the gas phase to the metal or alloy.

Affinity for carbon formation decreases with increasing temperatures. The temperature below which is affinity for carbon precipitation is called the Boudouard temperature. 15 Typical Boudouard temperatures are in the range up to 1000°C.

Carbon monoxide is the predominant cause of metal dusting corrosion, but hydrocarbons have also been reported to 20 cause metal dusting.

For kinetic reasons metal dusting only proceeds significantly at temperatures above a certain level, typically 25 more than 300°C.

The metal dusting corrosion phenomenon is thus observed predominantly in the temperature range of 300°C to 1000°C.

30 It is known that metal dusting is suppressed by the presence of H₂S in carbon monoxide containing gas. Meanwhile,

H₂S is poisonous to down-stream catalysts, H₂S content of the gas must be maintained at a very low level of 20 ppb.

5 In a number of industrial processes it is possible to use H₂S as protecting agent against metal dusting, if the down-stream processes accepts sulphur compounds or if the synthesis gas is passed through a CO₂ removal unit, wherein also H₂S is removed. In the latter case a failure in operation of the CO₂ removal unit will cause irreversible inactivation of down-stream catalysts, if these are susceptible to sulphur poisoning.

10 Thus, in a specific embodiment of the present invention H₂S is added to the synthesis gas up-stream to equipment being subjected to metal dusting, and subsequently selectively removed down-stream to the equipment.

15 In case the synthesis gas preparation section is tolerant to sulphur, the natural contents of sulphur in the hydrocarbon feed reformed is not removed and optionally supplementary H₂S may be added at any position upstream the equipment subjected to metal dusting to provide H₂S concentration in the synthesis gas being effective for the suppression of metal dusting down stream the reformer. H₂S is then selectively removed downstream to the equipment.

20 Thus, in another aspect the invention provides use of the adsorbent in the suppression of metal dusting of iron or nickel alloys in contact with carbon monoxide rich synthesis gas at a Boudouard temperature above 300°C, further containing both hydrogen, carbon dioxide and optionally steam. Thereby, an amount of a H₂S source is added to the

synthesis gas upstream the metal surface being in contact with the gas in a concentration being sufficient to suppress metal dusting. Subsequently, the sulphur compound is selectively removed at a temperature below 100°C downstream the metal surface.

The H₂S source may be either a gas containing H₂S or another sulphur compound, which at actual process conditions will decompose into H₂S, e.g. dimethyl disulphide.

10

The examples below demonstrate in more detail specific embodiments of the invention.

Example 1

15

Reference is made to Fig. 1. In this specific embodiment of the invention Fe and Ni containing alloys being exposed to synthesis gas downstream an autothermal reformer are protected against metal dusting. The synthesis gas produced in an autothermal reformer is well suited for the synthesis of synthetic liquid fuel in a down stream Fisher-Tropsch synthesis section.

20

The synthesis gas exiting an autothermal reformer (100) at 30 bar gauge contains by volume percent approximately H₂ 49, H₂O 20, CO 25, CO₂ 5 and CH₄ 1 corresponding to a Boudouard temperature of approximately 900°C. Potentially metal dusting will occur on Fe/Ni alloy surfaces between 300°C and 900°C if not protected.

25

CH₃SSCH₃ (110) is added to the synthesis gas effluent from the autothermal reformer. At the high temperature prevailing the CH₃SSCH₃ will thermally decompose and react with H₂

30

into H_2S . The amount of CH_3SSCH_3 added corresponding to approximately 1 ppm H_2S by volume in the resulting admixture (120).

5 The admixture is led through a series of heat exchange operations, where it during cooling supplies heat to other processes or streams. The first heat exchange operation (130) is a gas heated heat exchange reformer which receives heat from the admixture, while the admixture cools from 1050°C to approximately 600°C. The effluent from the gas heated heat exchange reformer (130) can in another lay-out be added to the synthesis gas from the autothermal reformer. The second heat exchange operation (140) is a boiler for steam production which receives heat from the admixture, while the admixture cools from 600°C to approximately 300°C. During cooling of the admixture in the heat exchange operations (130) and (140) Fe and Ni containing alloys being exposed to the synthesis gas trans-passes a temperature range 700-500°C, wherein severe metal dusting is observed. H_2S contained in the admixture protects heat recovery equipment against metal dusting down to a temperature of 300°C, where metal dusting for kinetic reasons does no longer occur. Under the kinetic limit for metal dusting heat recovery equipment is protected by low operating temperature and H_2S is no longer needed for this purpose.

The third heat exchange operation (150) is a boiler feed water preheater which receives heat from the admixture, while the admixture cools from 300°C to approximately 100°C. After the heat exchange operation (150), which brings the admixture to below the dew point of water, a first separation of process condensate is made (160). The

fourth heat exchange operation (170) is a second boiler feed water preheater which receives heat from the admixture, while the admixture cools from 100°C to approximately 40°C. After the heat exchange operation (170), separation
5 of process condensate is again made (180). The saturated synthesis gas outlet of the last process condensate separation (180) is brought to conditions above the dew point of water contained in the synthesis gas, in this example by simply re-heating of the synthesis gas in the heat exchange
10 operations (190) and (200). This re-heating must be done in case the downstream absorbent is susceptible to hydration.

Re-heated synthesis gas is introduced to a bed of sulphur absorbent (210), removing sulphur to a level below 5 ppb,
15 acceptable to most down stream syntheses.

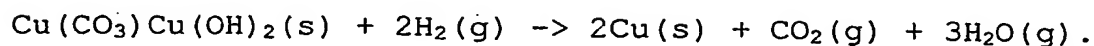
Example 2

This Example is not an example of the present invention. It illustrates the ease of reduction of mixed basic carbonates
20 exposed to a typical synthesis gas.

108 mg of mixed basic carbonates were loaded into a thermogravimetric reactor. In such a reactor the weight of the sample is continuously recorded. The reactor operates at
25 atmospheric pressure. The sample was exposed to reducing gas with the composition by volume percent H₂ 66.6 (balance), H₂O 2.2, CO 18.4, CO₂ 9.8 and Ar 3.0 for approximately 6 days at 45°C. Then the temperature was raised to 55°C and the experiment was run for another approximately 5
30 days.

Fig. 2 shows that at 45°C the weight of the sample of mixed basic carbonates is stable. Any reduction of mixed basic carbonates of copper would be accompanied by a weight loss through the reaction:

5



10

The mixed basic carbonates do not reduce in the synthesis gas at 45°C because the weight of the sample remains stable.

In line with the above reduction is seen, as a slowly decreasing weight, when the temperature is increased to 55°C.

15

Comparison Example 3

20

A test was made on desulphurisation of a synthesis gas at conditions typical of the outlet of the process condensate separation. The test was made on pure ZnO, more specifically on the catalyst type HTZ-3 available from Haldor Topsøe A/S, Denmark.

25

The test was carried out at accelerated conditions with a space velocity of approximately 10 times higher than a typical industrial space velocity and with a concentration of H₂S of approximately 5 times higher than what is needed to obtain a pronounced suppression of metal dusting corrosion.

30

Catalyst particles in the form of 4 mm cylinders were loaded in a plug flow reactor with an internal diameter of 5 mm. Thereafter, the test conditions were as follows:

Temperature 40°C
Pressure 20 bar gauge
Space velocity 25,000 Nm³ gas/m³ catalyst/h

- 5 Gas composition, percent by volume H₂ 70.48 (balance), H₂O 0.02 (approximately), CO 16.3, CO₂ 10.2, Ar 3.00, H₂S 3.2 ppm by volume, COS 70. ppb by volume.

10 The results of the test are shown in Fig. 3, where the outlet concentration of H₂S and COS are given versus the time on stream. Breakthrough of sulphur is seen already after about 50 hours of operation. Pure zinc oxide is, thus, not suitable for this kind of desulphurisation.

15 **Example 4**

 This is an example of the present invention, as a reduced Cu/ZnO compound has been used for the desulphurisation of synthesis gas rich in carbon monoxide and further containing both hydrogen, carbon dioxide and steam, and as the potential for methanol synthesis is far more than 1000 ppm.

20 Example 3 was repeated, however, reduced Cu/ZnO/Al₂O₃ was used as absorbent instead of ZnO, more specifically the catalyst type ST-101 available from Haldor Topsoe A/S, Denmark. The ST-101 was reduced prior to the test.

30 The results of the test are shown in Fig. 4, where the outlet concentration of H₂S and COS are given versus the time on stream. For Cu/ZnO/Al₂O₃ desulphurisation to the required low ppb level (5ppb) is obtained for about 200 hours, where after a breakthrough of COS is seen. Methanol synthesis was absent also during at short time test at 125°C after 66

hours of operation. When the test was terminated after 300 hours, H_2S was still below the detection limit of 5 ppb. The experiment was as mentioned before conducted with 10 times the normal space velocity and at 5 times the required H_2S level. Therefore, an estimated operation time for an industrial application will be at least 50 times the experimental run time. Thus, 200 hours of desulphurisation to below detection limit of COS and H_2S corresponds to 10000 hours of industrial operation below detection limit, which makes the process industrially useful.

Formation of COS can be explained by absorbed H_2S being converted by carbon monoxide in the feed gas to COS and hydrogen.

Example 5

This Example relates to whether the reduced Cu/ZnO compound catalyses the water gas shift reaction at the desulphurisation temperatures. The Cu/ZnO compounds are known to be excellent water gas shift catalysts. Therefore, it is important for the present invention to establish how low the desulphurisation temperature should be in order to limit the conversion of CO through the water gas shift reaction to insignificant levels.

The conversion of CO, through the water gas shift reaction, is possible because the synthesis gas to be desulphurised often is saturated with water and because the thermodynamic affinity for water gas shift, being an exothermic reaction, is large at low temperatures.

Considering the conditions of Example 1 the synthesis gas leaving the first water separator at 100°C will contain approximately 3% by volume of water. Therefore, the water gas shift reaction, in case it was catalysed by the sulphur absorbent, could lead to a large loss of CO from the synthesis gas.

The test on the water gas shift reaction was made on a Cu/ZnO/Al₂O₃ absorbent, more specifically the catalyst ST-101 available from Haldor Topsoe A/S, Denmark. Catalyst particles in the form of approximately 4 mm cylinders were loaded in a plug flow reactor with an internal diameter of approximately 5 mm. The catalyst was reduced, and thereafter the test conditions were as follows:

15

Temperature	148, 125 and 110°C
Pressure	20 bar gauge
Space velocity	5400-8500 Nm ³ /m ³ catalyst/h

20 Dry gas composition, percent by volume:
H₂ 72.50 (balance), CO 14.5, CO₂ 10.0, Ar 3.0.

Steam to dry gas ratio volume to volume: 0.028 - 0.090.

25 At 148°C and 125°C a significant conversion of CO through the water gas shift reaction was observed. At 110°C conversion was hardly to be observed any more.

30 By extrapolation of the test results it shows that at 100°C and at a typical industrial space velocity of 2500 Nm³/m³ catalyst/h, the conversion of CO will be only a fraction of

a per thousand. In other words, and for practical purposes, the Cu/ZnO/Al₂O₃ absorbent does not catalyse the water gas shift reaction at 100°C or below.

CLAIMS

1. A process for the selective removal of sulphur compounds from synthesis gas containing at least 5% carbon monoxide, at least 5% hydrogen and at least 0.5% carbon dioxide and (optionally) containing water in a concentration up to saturation at a pressure of at least 15 bar comprising contacting the synthesis gas at a maximum contact temperature of 100°C with an absorbent comprising Cu/ZnO compounds and activated with a reducing gas.
2. Process of claim 1, wherein the sulphur compounds comprise H₂S and COS.
3. Process according to any one of the preceding claims, wherein the synthesis gas contains H₂S in an amount effective for suppression of metal dusting of metals in contact with the synthesis gas within a temperature range between 300°C to Boudouard temperature of the synthesis gas.

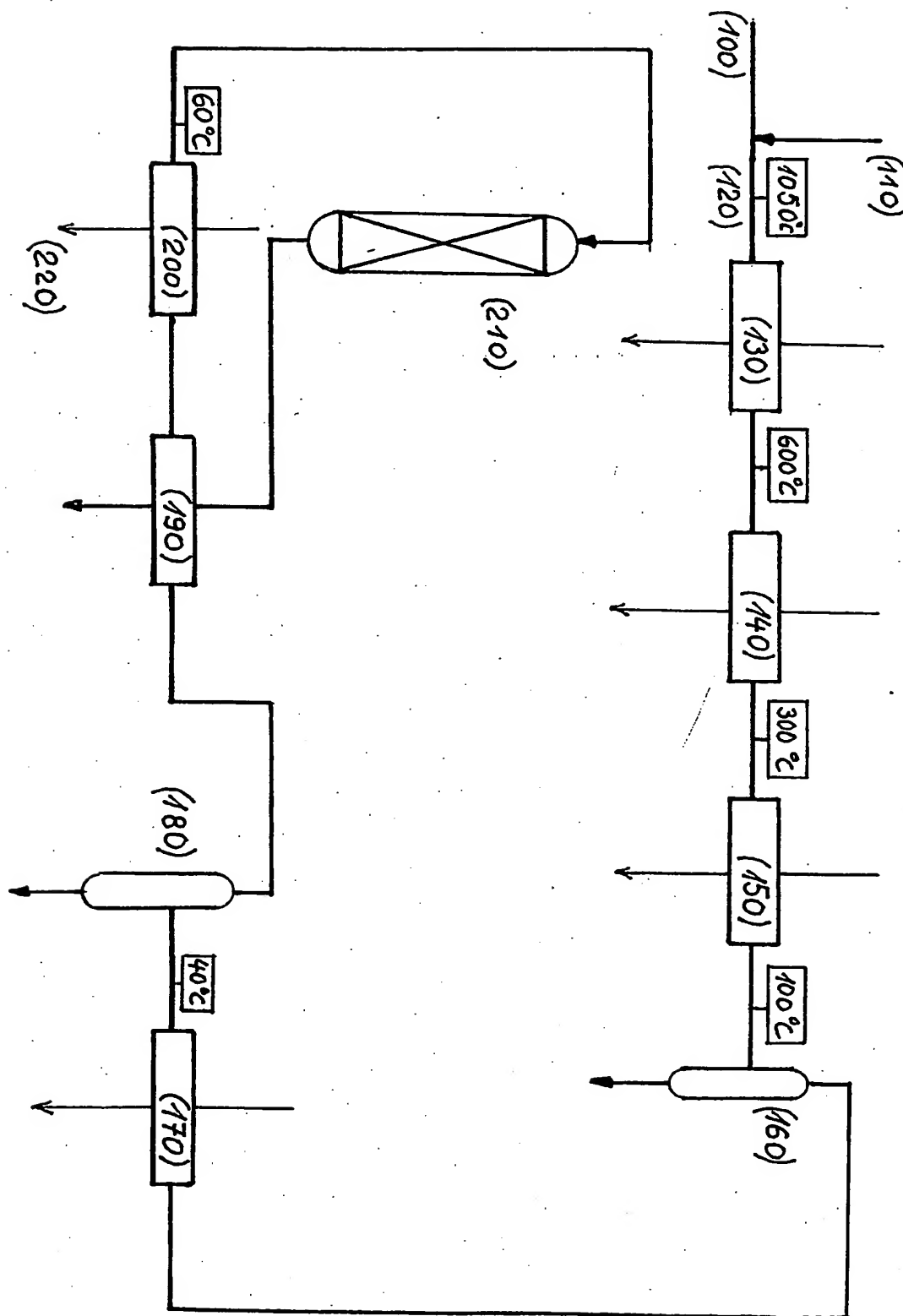
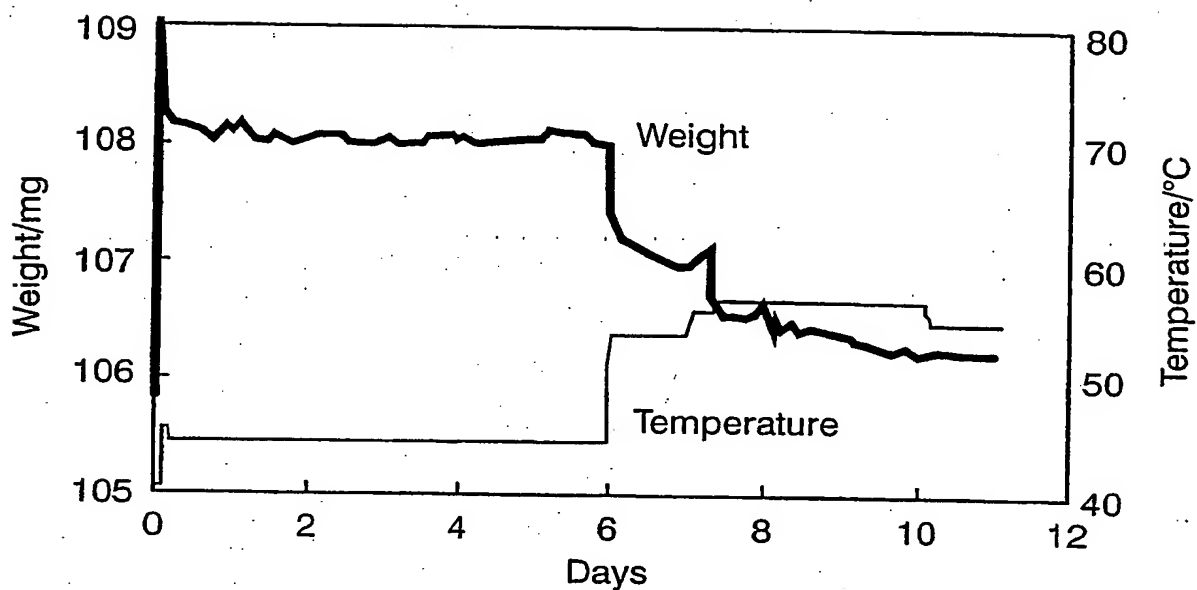


Fig. 1



Temperature programmed reduction of mixed basic carbonates

FIG. 2

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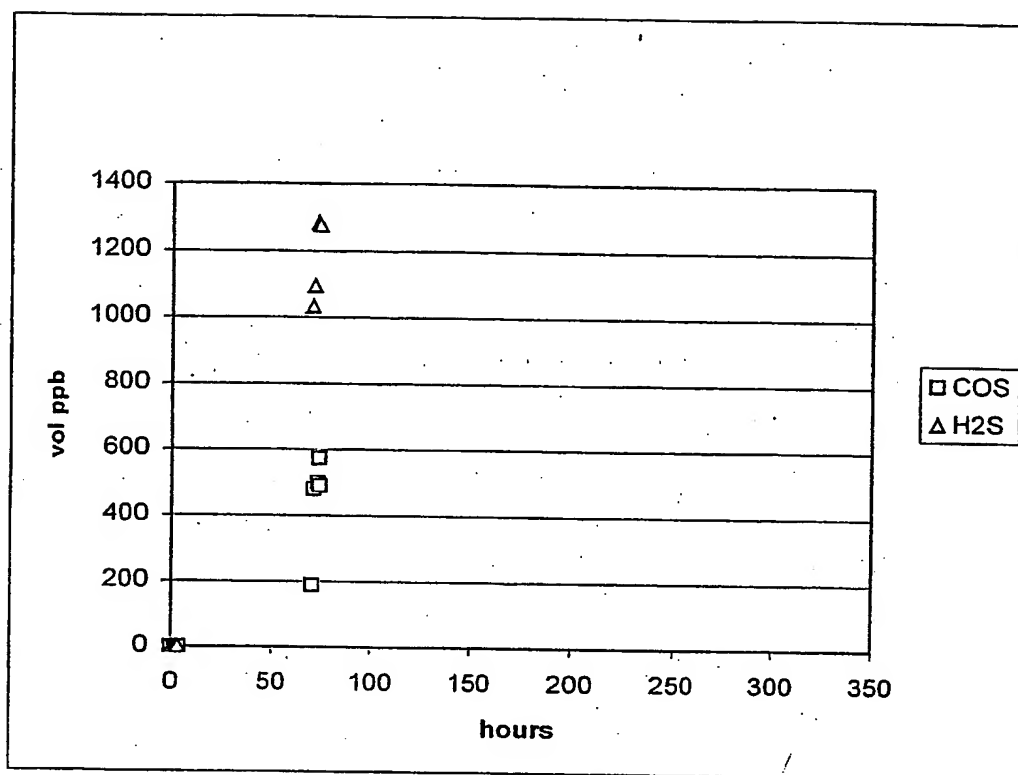
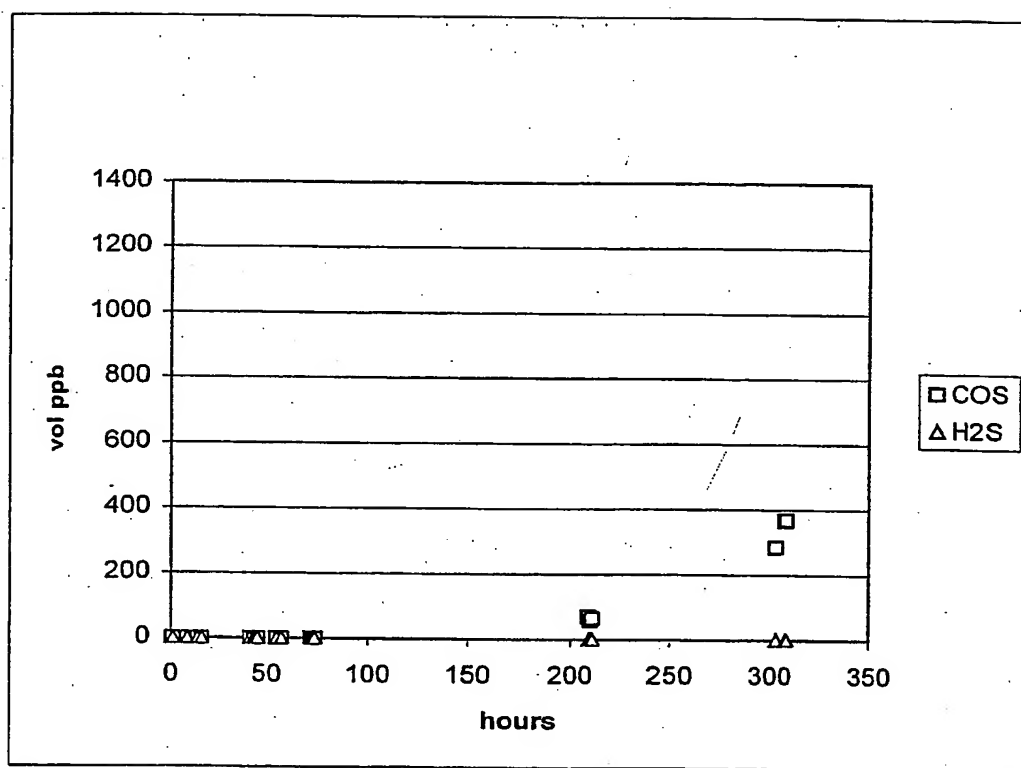


FIG. 3



Absorption of sulphur at 40°C and 21 bar
on Cu/ZnO/Al₂O₃